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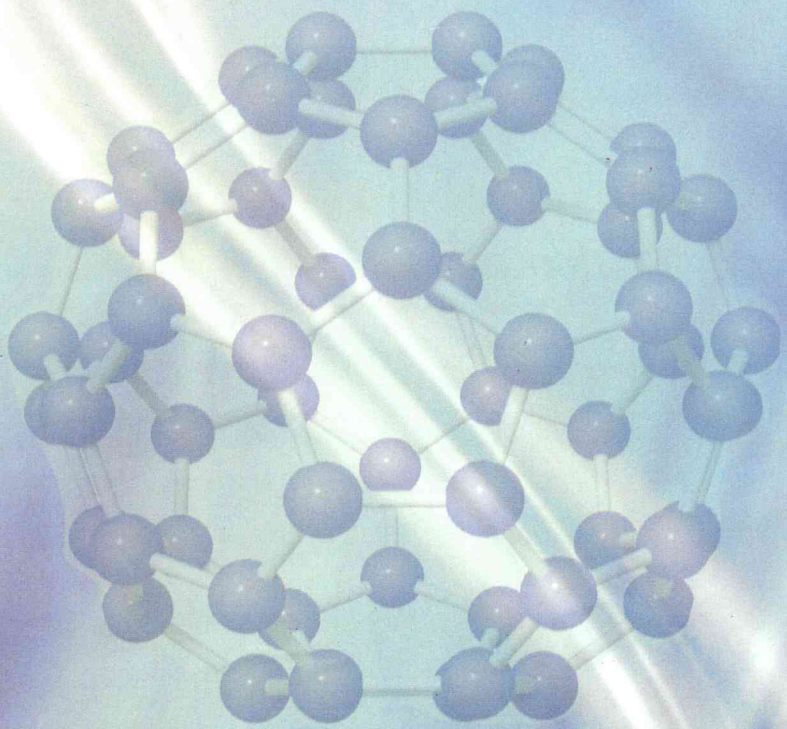

MATERIALS AND METALLURGICAL ENGINEERING DEPARTMENT
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Failure Analysis

Innovative Material

Corrosion Behavior of Material Based Zirconium Alloys

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Abstract

The corrosion behaviour of nanocrystal material based on Zirconium $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$, $Zr_{68}Cu_{14}Ni_{11}Al_7$, $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$ and $Zr_{53,1}Cu_{23}Ni_{18}Al_{5,9}$ have been analyzed. These alloys have been characterized thermally using Calorimeter Scanning Differential (DSC). DSC data show T_g value for $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$, $Zr_{68}Cu_{14}Ni_{11}Al_7$, and $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$ alloy are 379°C, 368°C and 392°C respectively, T_x value for $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$ is 428°C, 416 °C for $Zr_{68}Cu_{14}Ni_{11}Al_7$ and 431°C for $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$.Based on these data, alloys were heated at 390°C, 400°C and 410°C (temperature betwen T_g and T_x) during 1 hour. The phases of heated alloys were identified by X-ray diffraction. Phase identification was observed by matching method using formed phase table of JCPDF. While the crystal size is determined by Scherrer's equation. Identification result shows ZrO_2 phase with tetragonal and monoclinic structure and intermetallic phase Ni_7Zr_2, $Cu_{10}Zr_7$, Zr_2Ni, and $Ni_{10}Zr_7$ have been formed. The crystal size of oxide and intermetallic phases are in the range at 5 to 51 nm and 10-17 nm, respectively. Corrosion test is done using HNO_3 1 M solution for 5, 10 and 15 rninute. It's known that the highest Zr composition has the best corrosion resistant.

Keywords: Corrosion, Metallic Glass, Nanocrystal.

1. Introduction

Nanoscience has been developed rapidly in recenly years. Researchers try to observe material properties by reducing its size from bulk to nanocrystallite. This size reduction is important to find out all properties of the nanomaterials .[1]

Changing the size to nanometer scale has affected physical and chemical properties or even the biological properties. Nanocrystallite materials are defined materials that have crystal size 10 - 200 nm. [2]

Compared with bulk materials, nanocrystallite materials have several advantages. According to some research results, nanocrystal structure of material based of Zirconium has high oxidation resistance than amorphous structure or quasi - crystal. In crystallization process of amorphous material based of Zirconium, Addition one element [Cu], two components [Zr,Cu] and tri components [Zr,Cu,Al] as combination elements has increase its hardness value [3].

Zirconium alloys have been used in industrial environment, such as steel forming, porseline, and other ferrous combination. Other applications of these alloys are related to high temperature application and for several tools that need high corrosion resistance in acid environments. Zirconium alloys were used in reactor because of its corrosion resistance in increased temperature, strong, more ductile, and easy to form.

This present research is concern with temperature and the holding time of heated amorphous material in order to form nanocrystal structure. Composition of element combination also influences the properties and the result of material significantly.

Thermodynamically, amorphous structure could be change to crystal structure due to heat treatment process or other environment effects. This change is called phase transformation. According to J.W. Gibbs, there are two kind of phase transformation: spinodal decomposition, and nucleation and grain growth.

Crystallization is transformation pro-cess from amorphous to crystal phase. This process is occurred by changing liquid phase to solid state.

There are two crystallization mechanisms: nucleation and crystal growth. Fig. 1 shows hypotectic diagram to explain crystallization phenomena.

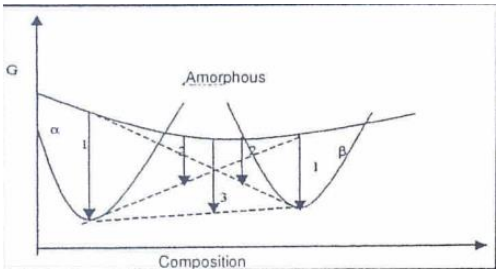

Fig. 1 Hypotectic diagram for phase transformation from amorphous to crystal phase

According to hypotectic diagram in Fig. 1, there is several possible crystallization processes from amorphous to crystal phase, which are:

1. Polymorphous crystallization, which is crystal formation from amorphous phase with the same chemical composition and minimum free energy, as shown in line no. 1 in Fig. 1 (amorphous → α atau amorphous → β).
2. Primer crystallization, which is crystal formation from amorphous phase with amorphous residue, as shown in line no. 2 in Fig. 1. (amorphous → α + amorphous atau amorphous → β + amorphous).
3. Eutectic crystallization, which is crystal formation from amorphous phase with different chemical composition, as shown in line no. 3 in Fig. 1 (amorphous → $\alpha + \beta$).[4]

Experimental

This research use followed experiment procedures:

1. Thermal characterization was done by DSC (Differential Scanning Calorimeter) mea-surement. According to DSC data, it can be observed T_g and T_x values.
2. Zr-Cu-Ni-A1 alloys (with variation composition) were heated under non vaccum furnace with various temperatures (390-410) and an hour holding time. The alloys were characterized by XRD. From XRD data, it can be analyzed phases formed in the samples and the crystallite size.
3. Corrosion resistance can be observed by calculate the corrosion rate.

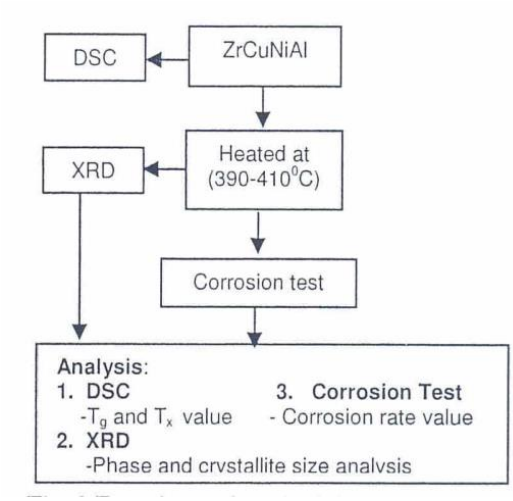

Fig. 2 Experimental methodology

Result and Discussion

DSC Result

Fig. 3 shows DSC data for Zirconium Alloys with different composition. Glass transition temperature (T_g) and crystallization temperature (T_x) can be observed from DSC data. T_g value of $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$, $Zr_{68}Cu_{14}Ni_{11}Al_7$, and $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$ are 379, 368 dan 392 respectively. Whereas T_x value for $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$, $Zr_{68}Cu_{14}Ni_{11}Al_7$, and $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$ are 428, 416 and 431 respectively.

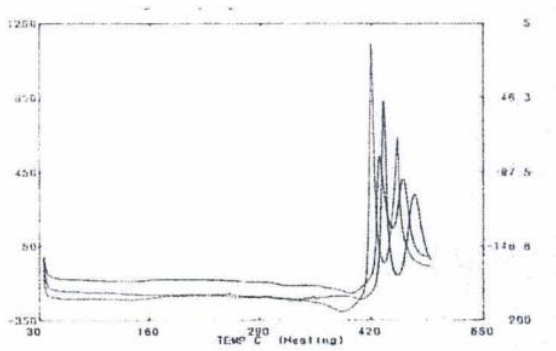

Fig. 3 DSC curve for heat rate 5°C/minutes. The green line for $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$, the blue one for $Zr_{68}Cu_{14}Ni_{11}Al_7$,and the red one for $Zr_{69,5}Cu_{12}Ni_{11}Al_{7,5}$.

XRD Result

Fig. 4 shows diffraction pattern for $Zr_{53.1}Cu_{23}Ni_{18}Al_{5,9}$ alloy shows dominan phase which formed in the alloy is ZrO_2 phase with tetragonal structure and Zr_3O_{1-x} phase with rhombohedra1 structure.

Intermetallic phase $Ni_{10}Zr_7$ with orthorombic structure was observed at temperature 410 °C .

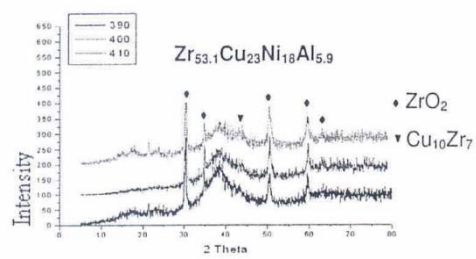

Fig. 4. XRD pattern for $Zr_{53.1}Cu_{23}Ni_{18}A1_{5,9}$ alloy after heat treatment for 1 hour with various temperatures

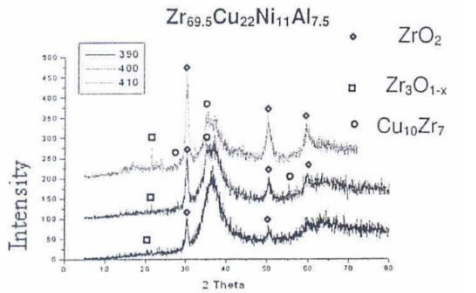

Fig.5. XRD pattern for $Zr_{69.5}Cu_{22}Ni_{11}Al_{7,5}$ alloy after heat treatment for 1 hour with various temperatures

Diffraction pattern for $Zr_{69.5}Cu_{22}Ni_{11}Al_{7,5}$ alloy is shown in Fig.5. Oxide phase formed in alloys is ZrO_2 (tetragonal structure). Whereas the intermetallic phase are $Cu_{10}Zr_7$ (Orthorombic) and Ni_7Zr_2 (monoclinic) respectively at temperature 400 °C dan 410 °C. Intermetallic phase has the smallest free energy so that it can easily be formed.[5]

Intermetallic phase $Cu_{10}Zr_7$ formed in this alloy indicated that Cu atom diffusion has important role for crystallization process. Cu atoms have high diffusion ability in alloy. [6]

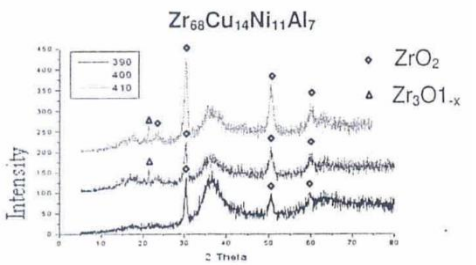

Fig. 6. XRD pattern for $Zr_{68}Cu_{14}Ni_{11}Al_7$ alloy after heat treatment for 1 hour with various temperatures

Fig. 6 shows diffraction pattern for $Zr_{68}Cu_{14}Ni_{11}Al_7$ alloy. ZrO_2 phase formed tetragonal structure and monoclinic. It was also formed oxide phase Zr_3O_{1-x}.

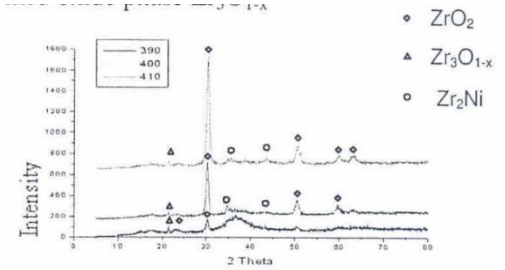

Fig. 7. XRD pattern for $Zr_{68}Cu_{14}Ni_{11}Al_7$ alloy after heat treatment for 1 hour with various temperatures

Fig. 7 shows XRD pattern for $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$ alloy, Beside there is ZrO_2 phase (tetragonal), it also form intermetallic phase Zr_2Ni(tetragonal) at temperature 410 °C.

Crystal Size

Crystal size of the phases found in alloys was calculated using Scherrer's formula. Full Width at Half Maximum (FWHM) was observed by assisting fitting software. The change in crystal size indicates the process of crystallization

Fig. 8 Relation between crystal size and temperature of $Zr_{53.1}Cu_{23}Ni_{18}A1_{5,9}$ alloy

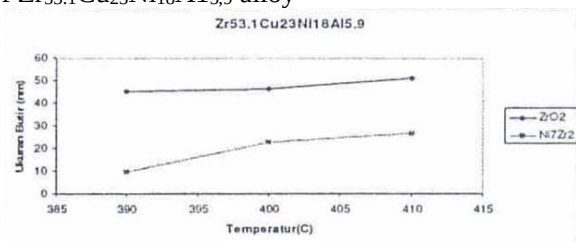

Fig. 9 Relation between crystal size and temperature of $Zr_{68}Cu_{14}Ni_{11}Al_7$ alloy

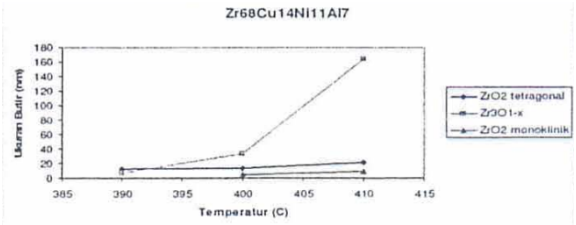

Fig. 8-9 show the dependence of crystal size to heat treament temperature

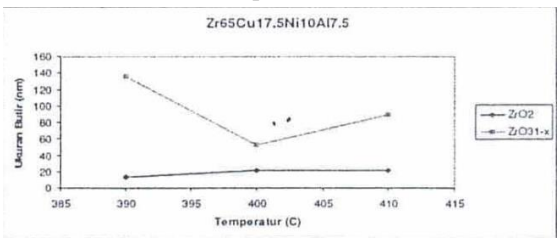

Fig. 10 Relation between crystal size and temperature of $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$

Crystal size of oxides phase ZrO_2 increase when heat temperature was increased. This phenomenon was not occured in Zr_3O_{1-x}. The crystal size decrease while the heat temperature increased. It might be caused by transformation to another phases or the disorder of the crystallite phase.

Corrosion Test Result

Corrosion rate of the material based on zirconium alloys was determined by loss weight method. The result of corrosion test in this precent research were shown in Fig.12. The materals were heated at 390 °C, 400 °C and 410 °C in HNO_3 1 M solution for 5, 10 and 15 minutes.

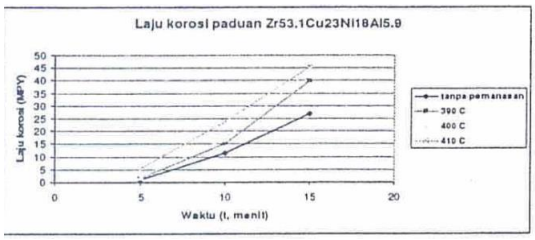

Fig. 11. The relation between corrosion rate and the various temperature and time of $Zr_{53.1}Cu_{23}Ni_{18}A1_{5,9}$ alloy

Fig. 11 shows the increasement of corrosion rate while increasing heat temperature. This is due to the alloy without heat treatment has amorphous phases. As known that amorphous state has high corrosion resistance. [7]

Increasing temperature can cause higher thermal energy received in amorphous alloys. This mechanism allows nu-

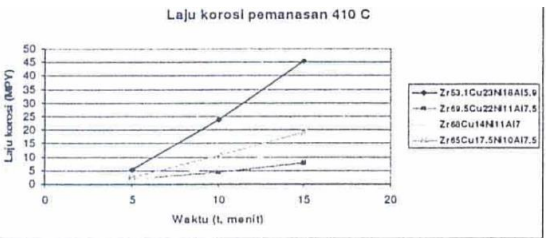

Fig. 12 The relation between corrosion rate and the various temperature and time of Zr-Cu-Ni-Al alloy (variuos composition) at 410 °C

cleation from liquid to grow and fill the lattice vacancy that might be present. This thermal energy is used to grow the crystal until end of transformation. The higher heat temperature the larger crystal size that can be grown.

From Fig. 12, corrosion rate value can be sorted from the low one to the higher one of the alloys, which is $Zr_{69.5}Cu_{23}Ni_{ll}A1_{7.5}$, $Zr_{68}Cu_{14}Ni_{11}A1_7$, $Zr_{65}Cu_{17.5}Ni_{10}A1_{7.5}$, dan $Zr_{53.1}Cu_{23}Ni_{18}A1_{5,9}$ respectively. Zr and Al composition in the alloy may influence corrosion resistance. These elements might increase corrosion resistance due to the formation of thin film ZrO_2 and Al_2O_3 that protect the alloy from further oxidation. $Zr_{69.5}Cu_{22}Ni_{11}Al_{7,5}$ alloy has better corrosion resistance compared with $Zr_{68}Cu_{14}Ni_{11}Al_7$, $Zr_{65}Cu_{17,5}Ni_{10}Al_{7,5}$ and $Zr_{53.1}Cu_{23}Ni_{18}Al_{5,9}$ alloy.

Metallic glass composition has also affected corrosion process. The higher Zr and Al composition the higher corrosion resistance of the alloys.

Conclusion

1. Average crystal size of oxide phases are 5-51 nm and for intermetallic crystals are 10-17 nm.
2. Corrosion rate value increase as well as the increase of heat treatment temperature.
3. Metallic glass composition may influence corrosion process. The higher Zr and Al composition in alloys, the higher corrosion resistance.

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